

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant	:	<b>Pradeep K. Agarwal et al</b>	
Filed	:	<b>Herewith</b>	
For	:	<b>SYSTEM FOR RECOVERY OF SULFUR AND HYDROGEN FROM SOUR GAS</b>	
Docket No.	:	<b>W02.PAT-12</b>	

**PRELIMINARY AMENDMENT**

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sirs:

Please enter this Preliminary Amendment:

IN THE CLAIMS

Please cancel claims 1 – 23.

Please add the following claims:

--24. An apparatus for converting H<sub>2</sub>S to elemental sulfur and hydrogen, the apparatus comprising:

conversion means for receiving H<sub>2</sub>S and for converting H<sub>2</sub>S to elemental sulfur and hydrogen at a predetermined temperature less than approximately four hundred (400°) degrees C.--

--25. The apparatus of claim 24 wherein the conversion means is a nonthermal plasma corona reactor.--

--26. The apparatus of claim 1 and further comprising:

adsorbent means positioned within a fluidized bed for removing at least a portion of  $H_2S$  from a natural gas stream; and  
means for providing the removed  $H_2S$  to the conversion means.--

--27. The apparatus of claim 26 wherein the adsorbent means includes a first adsorbent having a first predetermined temperature and second adsorbent having a second predetermined temperature.--

--28. The apparatus of claim 27 wherein the first adsorbent and the second adsorbent are a molecular sieves.--

--29. The apparatus of claim 28 wherein the second predetermined temperature is greater than the first predetermined temperature.--

--30. A method for converting  $H_2S$  to elemental sulfur and hydrogen, the method comprising:  
providing a nonthermal plasma corona reactor;  
introducing the  $H_2S$  into the nonthermal plasma corona reactor; and  
converting the  $H_2S$  to elemental sulfur and hydrogen at a predetermined temperature.--

--31. The method of claim 30 wherein the predetermined temperature is less than approximately four hundred ( $400^\circ$ ) degrees C.--

Respectfully submitted,

PRADEEP K. AGARWAL et al

By: 

Emery L. Tracy, Reg. No. 34,081

P.O. Box 1518

Boulder, Colorado 80306

Phone: (303) 443-1143 Fax: (303) 443-1415

To: Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

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Applicant:  
**UNIVERSITY OF WYOMING et al**

Priority Date:  
**24 March 2000 (24.03.00)**

For **SYSTEM FOR RECOVERY OF SULFUR AND HYDROGEN FROM SOUR  
GAS**

### AMENDMENT

Sir:

In response to the Written Opinion mailed on 16 January 2001, the following amendments are made to the present application:

Applicant hereby submits replacement sheets for the entire application. The changes to the originally filed applications are as follows:

### SUMMARY

Page 4, lines 3 – 10, has been amended to better define the present invention.

Page 4, lines 11 – 23 have been removed.

Page 4, lines 28 – 34, and page 5, lines 1 – 4, have been removed.

Page 5, lines 5 – 17, has been amended to better define the present invention.

Page 5, lines 18 – 25, has been removed.

### CLAIMS

Claim 1 has been amended to better define the present invention.

Claim 3 has been amended to better define the present invention.

Claim 4 has been amended to better define the present invention.

Claim 5 has been amended to correct a typographical error.

Claim 17 has been amended to correct a typographical error.

Claim 18 has been amended to better define the present invention.

Claim 19 has been amended to better define the present invention.

Claim 20 has been amended to correct a typographical error.

### REMARKS

The Examiner stated that claims 12 and 13 do not meet the criteria novelty set forth in PCT Article 33(2) because the claimed subject matter is anticipated by the article titled "Hydrogen Sulfide Waste Treatment by Microwave Dissociation" by Harkness et al. Applicant respectfully disagrees.

The Harkness et al article describes high-frequency induced plasmas – such as those generated by microwaves and radio frequencies (RF). The present invention claims a new and improved approach that overcomes limitations of high-frequency induced plasmas such as those generated by microwaves and radio frequencies (RF) for dissociation of hydrogen sulfide into sulfur and hydrogen. The main differences between technologies employing microwave plasma and the pulsed corona and silent barrier discharge are fundamentally and operationally different. The key issues of difference include electrode geometry, method of generation of the plasma, operating pressure, and energy efficiency.

The Examiner also stated that the second full paragraph under the header "Background" sets forth that the gas is at a temperature ranging from 50 to 300 °C." It should be noted that the gas entering the pulsed corona plasma reactor of the present invention can be at ambient air temperature or even lower. The temperature of the gas need not be between 50 and 300 °C for the process to work; the inlet gas temperature can, in fact, be below 0 °C depending on the handling and processing of the gas upstream of the corona reactor.

The Examiner stated that claims 1 – 23 do not meet the criteria for an inventive step set forth in PCT Article 33(3) because the claimed subject matter is obvious from Canadian Patent 675,292 to Milton in view of "Hydrogen Sulfide Waste Treatment by Microwave Dissociation" by Harkness et al. The Examiner stated that the differences between the Applicants' claims and the Milton patent is that the Applicants' claims call for the provision of a second adsorbent bed which further purifies the partially cleaned natural gas exiting the first adsorbent bed, however, it is submitted that this difference would have been obvious to one of ordinary skill in the art at the time the invention was made because of the expected advantage of removing any contaminants still remaining in the gas that managed to escape removal in the previous adsorption bed. Applicant respectfully disagrees.

The present invention employs fluidized beds both for adsorption and regeneration of the adsorbent. In fixed-beds – the operating regime in the invention of Milton - fluid flows through a bed of packed solid particles – the solids are then stationary. For fluidization to

occur, the drag due to the upward flow of the fluid must balance the weight of the bed particles. The larger the particles, the more difficult it is to suspend them in a gas stream. The fluid flow rate must also be higher than in the fixed-bed regime; in fact, the minimum fluidizing velocity defines the transition between fluidized- and fixed-bed operation. Once the bed of solids is fluidized, the solids acquire the gross flow characteristics of a liquid. Furthermore, the present invention employs a fluidized bed regenerator instead of a packed bed as in the Milton patent. The advantages of using a fluidized bed instead of a packed bed for regeneration of the contaminants loaded adsorbent are that high heat transfer rates to immersed heat-exchange equipment, leading to not only smaller equipment but also efficient utilization of energy.

Furthermore, the Examiner stated that the difference between the applicants' claims and the Milton patent is that the Applicants' claims 10 - 14, 18, and 23 call for the passage of hydrogen sulfide rich regeneration gas into a plasma reactor at a temperature less than 400 °C (752 °F) so as to dissociate the hydrogen sulfide into hydrogen and sulfur. Applicant respectfully disagrees.

There are many differences between the present invention and the Milton patent. The Milton patent employs a packed bed of adsorbent, whereas the present invention employs a fluidized bed to exploit advantages of such mode of operation, such as ease of adsorbent transportation from the adsorber to the regenerator. In the Milton patent there are two packed beds employed. These beds are switched alternately, to serve as adsorber and regenerator. Once the first bed is saturated with contaminants during the adsorption stage, the sour gas is switched to the second bed which at this stage has fresh adsorbent. The first bed is then regenerated and cooled. When the second bed is saturated with contaminants, the sour gas is switched back to the first bed, which by now must have cooled down to the desired adsorption temperature. It should be noted that the bed that serves as the regenerator must first be heated to the desorption temperature, and then cooled to adsorption temperature before it can be reused again for treatment of a fresh feed of sour gas. This process is time and energy consuming.

In the present invention the adsorbers and regenerators are maintained at their optimum operating temperature all the time. The regenerated adsorbent is recycled continuously thereby saving time and increasing throughput.

In the Milton patent, the purge gas for regeneration must be preheated before entering the desorption bed. This requires a separately installed heater. In addition, the bed of solids in the regenerator is also heated indirectly by an immersed coil which uses heated oil. By

contrast, in the present invention heat is supplied to the regenerator by burning some of the gas recovered from the pulsed corona plasma reactor. A special feature of heat addition to the regenerator is the use of pulse combustor tubes immersed in the bed of solids to be regenerated. The heating is accomplished using hot flue gases. The present invention does not require pre-heating the purge gas externally prior to its introduction into the regeneration bed. This is definitely a much more economically favorable approach.

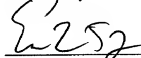
The Examiner objected to the description under PCT Rule 66.2(a)(v) as lacking clarity under PCT Article 5 because it fails to adequately enable practice of the claimed invention because the submission that the second adsorbent means mentioned on page 4, lines 7 - 10, in the specification purifies the gas at a temperature of 100 to 300 °C mentioned on page 4, lines 17 - 19, in the specification appears to be in error in as much as page 6, lines 23 - 26, of the specification sets forth that the adsorbent is regenerated at 100 to 300 °C.

It should be noted that the purification of gas refers on page 4, lines 7 - 10, refers to the first predetermined temperature and the specification on page 6, lines 23 - 26, refer to the second predetermined temperature.

The Examiner objected to claims 8, 9, and 22 as lacking clarity under PCT Rule 66.2(a)(v) because practice of the claimed invention is not enabled as required under PCT Rule 5.1 (a) for the reasons set forth in the immediately preceding paragraph. Claims 8, 9, and 22 all report a significantly higher temperature (i.e. 100 to 300 °C) for the further purification of the contaminated natural gas than the 20 to 60 °C reported on page 4, lines 15 - 17; page 5, lines 19 - 22; and page 6, lines 18 - 22 in the specification. The Examiner stated that it appears that the Applicants are reciting the regeneration temperature in claims 8, 9, and 22 rather than the purification treatment temperature.

Applicant has amended the claims to better define the invention of the present application. Claims 8, 9, and 22 refer to the second predetermined temperature of the second adsorbent means.

Respectfully submitted,



Emery L. Tracy, Reg. No. 34,081  
P.O. Box 1518  
Boulder, CO 80306  
(303) 443-1143

## SYSTEM FOR RECOVERY OF SULFUR AND HYDROGEN FROM SOUR GAS

The present application is a continuation of pending provisional patent application  
Serial No. 60/125,962, filed on March 24, 1999, entitled "System For Recovery Of Sulfur  
5 And Hydrogen From Sour Gas Using A Plasma Reactor".

BACKGROUND OF THE INVENTION1. Field of the Invention

This invention relates generally to a process for removal of hydrogen sulfide from  
10 a gaseous stream and the subsequent recovery of hydrogen and sulfur from the hydrogen  
sulfide and, more particularly, it relates to removal of  $H_2S$ ,  $CO_2$ , and  $H_2O$  from a sour  
natural gas stream in a fluidized bed adsorber followed by the conversion of  $H_2S$  to  
elemental sulfur and hydrogen in a corona reactor.

15 2. Description of the Prior Art

The proven reserves of natural gas in the United States are of the order of 170  
trillion cubic feet; taking data from various exploration programs into account, the natural  
gas resource base may be inferred to be close to 1118 trillion cubic feet. About twenty  
(20) trillion cubic feet of the proven reserves of natural gas contain significant amounts of  
20  $H_2S$ ,  $CO_2$ , and  $H_2O$  and other sulfur-containing contaminants. The sulfur must be  
removed from such streams to enable users to comply with environmental regulations.  
Moisture removal is necessary since the presence of moisture leads to the formation of  
hydrates, which through increasing the pressure drop along the transmission pipeline,  
decrease transmission capacity.  $CO_2$  is an undesirable diluting gas, which lowers the  
25 heating value of natural gas. Presence of moisture and  $H_2S$  is also a major factor in  
corrosion of equipment.

Processes for removal of  $H_2S$  from a gas stream are based on two principal  
mechanisms: absorption by regenerable solvents and adsorption on a bed of solids.  
Processes based on absorption often involve the use of one of the several amine solutions  
30 such as monethanolamine, diethanolamine, and triethanolamine, followed by thermal  
regeneration of the solvent to recover acid gases and the amine solution.

Most adsorption processes employ fixed beds, but moving and fluidized beds are  
also used. Adsorbent materials for  $H_2S$  removal include molecular sieves, iron oxide, zinc  
oxide, zinc titanate, tin oxide, and zinc ferrite. Molecular sieves have excellent selective

adsorption properties for polar compounds such as H<sub>2</sub>O, CO<sub>2</sub>, H<sub>2</sub>S, SO<sub>2</sub>, COS, and mercaptan. Since molecular sieves are designed to strongly attract and retain specific gas components, they are well suited for thermal-swing regeneration in a temperature swing adsorption cycle. Regeneration produces an enriched stream of the adsorbate and a revitalized sorbent for reuse.

Conversion of hydrogen sulfide to recover sulfur is often accomplished via the Claus process. The Claus process was invented in 1883 by Carl Friedrich Claus, a London Chemist, and was put into industrial-scale operation in the 1950's in the United States. A typical Claus sulfur-recovery plant consists of two major process stages. Stage one consists of a combustion furnace, waste heat boiler, and a sulfur condenser. Stage two is comprised of a series of catalytic converters numbering between one and four units. Each of the catalytic converters is equipped with a re-heating unit, catalyst bed, and a sulfur condenser. Hydrogen sulfide is converted to sulfur in the Claus process by two principal reactions: combustion of part of the hydrogen sulfide to sulfur dioxide and subsequent reaction of sulfur dioxide with hydrogen sulfide over a catalyst to produce sulfur and water.



Sulfur recovery up to 97% is achievable by employing multiple catalytic converters.

Conversion of H<sub>2</sub>S to elemental sulfur can also be achieved by dissociation of H<sub>2</sub>S by energetic electrons. This can be implemented by employing a number of nonthermal plasma processes, which include corona, dielectric barrier, microwave, and radio-frequency discharges. In a pulsed corona reactor, high-voltage pulses produce short-lived microdischarges, which preferentially accelerate the electrons without imparting significant energy to the ions. This results in improvement in power consumption and energy saving potential. In addition, since most of the energy applied goes to accelerating the electrons rather than the massive ions, larger reactor volumes are possible because the high energy electrons are capable of filling larger volumes.

Existing methods for removal of H<sub>2</sub>S by adsorption use fixed bed technology.

Fixed beds suffer from the inherent problem of slow response to changes in gas temperature. By comparison, fluidized-bed adsorption processes offer excellent gas-solid contact, fast kinetics, and steady operation. However, stresses induced by rapid temperature swings and fluidization have hampered efforts to use fluidized beds for adsorption.



Most industrial sulfur recovery processes are based on the Claus process, which entails partial combustion of  $H_2S$  stripped from the natural gas stream to form  $SO_2$ , Reaction (1). Elemental sulfur is recovered by the reaction of the remaining  $H_2S$  with  $SO_2$  as shown in Reaction (2). Thermodynamic constraints of Reaction (2) limit the conversion of  $H_2S$  in a single stage catalytic converter (to about 0.7) and, hence, the thermal recovery of elemental sulfur from the Claus furnace (operated at around 2400° F). In order to increase the efficiency of sulfur recovery, the effluent gases from the Claus furnace are cooled to recover sulfur and then contacted over a number of packed-bed catalytic converters at lower temperatures. Depending on the number of stages employed, recovery efficiencies vary between 90% and 98%. For optimum operation, the composition of the gases in the Claus process must be maintained such that the  $H_2S/SO_2$  ratio is 2:1. Even after several conversion stages, 2000-3000 ppm of  $H_2S$  and  $SO_2$  may remain in the effluent gas from the Claus process, posing environmental compliance problems. Customarily, an additional tailgas cleanup unit is employed to ensure that the final overall sulfur recovery exceeds 99%. Two such processes for tailgas cleanup are the Shell Claus off-gas treatment (SCOT) process and the Superclaus process. The SCOT tailgas cleanup process is the most widely used. However, an "add-on" SCOT plant may cost as much as the parent Claus plant itself.

Alternatively, a Superclaus unit may be introduced as the last stage in the series of catalytic converters. The process is based on selective oxidation of the unconverted  $H_2S$  to elemental sulfur, in the presence of a catalyst. Although both SCOT and Superclaus processes can improve sulfur recovery efficiency, the cost of installation of plant may not be offset by the sulfur recovered. Moreover, both processes fail to recover hydrogen, a valuable resource that may improve the overall economics of sulfur removal.

The mechanism of electron-impact assisted dissociation of  $H_2S$  occurs according to the following reactions:



Unstable atomic sulfur and hydrogen formed in reaction (3), recombine to stable  $H_2$  and  $S$  as shown in reactions (4) and (5). In an electrical discharge reactor, the reactivation of  $H_2$  and  $S$  leads to reformation of  $H_2S$ . This has an impact on the conversion and energy efficiency of the process.

SUMMARY

The present invention is a device for removing contaminants from a natural gas stream. The device comprises a first adsorbent positioned within a first fluidized bed operating at a first predetermined temperature for removing at least a portion of the contaminants from the natural gas stream and creating a sweetened natural gas stream and a spent sorbent. A second adsorbent is positioned within a second fluidized bed operating at a second predetermined temperature for receiving the spent sorbent from the first adsorbent means with the second adsorbent means removing the contaminants from the spent sorbent and circulating regenerated sorbent to the first adsorbent means.

The present invention additionally includes an apparatus for converting  $H_2S$  to elemental sulfur and hydrogen. The apparatus comprises conversion means for receiving  $H_2S$  and for converting  $H_2S$  to elemental sulfur and hydrogen at a predetermined temperature less than approximately four hundred ( $400^\circ$ ) degrees C.

The present invention further includes a method for removing  $H_2S$  and other contaminants from a natural gas stream and converting  $H_2S$  to elemental sulfur and hydrogen. The method comprises providing first adsorbent means, positioning the first adsorbent means within a fluidized bed at a first predetermined temperature, introducing the natural gas stream to the first adsorbent means thereby removing at least a portion of the  $H_2S$  and other contaminants from the natural gas stream and creating a sweetened natural gas stream and a spent sorbent, providing second adsorbent means, positioning the second adsorbent means within a fluidized bed at a second predetermined temperature, introducing the spent sorbent from the first adsorbent means to the second adsorbent means thereby removing the contaminants from the spent sorbents and creating a regenerated sorbent, recirculating the regenerated sorbent from the second adsorbent means to the first adsorbent means, providing a nonthermal plasma reactor, introducing the removed contaminants from the second adsorbent means to the nonthermal plasma reactor, and converting the  $H_2S$  to elemental sulfur and hydrogen at a third predetermined temperature.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a perspective view illustrating a system for recovery of sulfur and hydrogen from sour gas, constructed in accordance with the present invention, including (1) removal of  $H_2S$ ,  $CO_2$ , and  $H_2O$  from a sour natural gas stream and sorbent

regeneration and (2) conversion of  $H_2S$  to elemental sulfur and hydrogen in a corona reactor; and

FIG. 2 is a schematic diagram illustrating the process for (1) removal of  $H_2S$ ,  $CO_2$ , and  $H_2O$  from a sour natural gas stream and sorbent regeneration and (2) conversion of  $H_2S$  to elemental sulfur and hydrogen in a corona reactor, constructed in accordance with the present invention.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

As can be understood by those persons skilled in the art, the basic concepts of the present invention can be embodied in a variety of ways. The present invention involves both processes and devices to accomplish the improved processes. In the present application, the processes are discussed in detail. Systems and devices to be established under the invention are described as items inherent to utilization of such processes. To the extent some devices are disclosed, it should be understood that these not only accomplish certain methods, but also can be varied in a number of ways. Importantly, as to all of the foregoing, all of these facets should be understood to be encompassed by the disclosure herein.

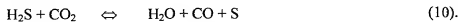
As illustrated in FIG. 1, the present invention comprises the removal of  $H_2S$ ,  $CO_2$ ,  $H_2O$ , and other sulfur-containing contaminants from natural gas streams employing a fluidized bed adsorber and recovery of elemental sulfur and hydrogen in a corona reactor at low temperatures, preferably less than approximately four hundred ( $400^\circ$ ) degrees C. The process consists of two steps. The first step is the removal of  $H_2S$ ,  $CO_2$ , and  $H_2O$  from a sour natural gas stream and sorbent regeneration. This step is accomplished using the concept of temperature swing adsorption. The contaminants in the natural gas are adsorbed on molecular sieves in fluidized beds operated at low temperatures, preferably between approximately twenty ( $20^\circ$ ) degrees C and approximately sixty ( $60^\circ$ ) degrees C. The spent sorbent is circulated to a high temperature, preferably between approximately one hundred ( $100^\circ$ ) degrees C and approximately three hundred ( $300^\circ$ ) degrees C, fluidized bed regenerator and the gas stripped from the sorbent in the regenerator is used for sulfur and hydrogen recovery.

The second step is the conversion of  $H_2S$  to elemental sulfur and hydrogen in a corona reactor at a temperature less than approximately four hundred ( $400^\circ$ ) degrees C. The  $H_2S$ ,  $CO_2$ , and  $CH_4$  from the regenerator will form the primary feed to a corona

reactor. Recovery of elemental sulfur and hydrogen from H<sub>2</sub>S in a nonthermal plasma reactor is based, primarily, on the following reactions:



The emphasis is on the dissociation of H<sub>2</sub>S according to Reaction (6). Formation of sulfur occurs by Reaction (7). Reactions (8) and (9) are responsible for formation of hydrogen. Since the feed gas stream to the corona reactor consists of H<sub>2</sub>S and CO<sub>2</sub>, the following reaction can also take place:



The approach herein has a distinct advantage in that the fuel value of H<sub>2</sub>S is transformed to CO and H<sub>2</sub>; this synthesis gas can actually be burnt to meet the energy requirements of the process. While CO<sub>2</sub> also leads to the formation of COS, its production can be minimized by choice of proper operating conditions.

Referring now to FIG. 2, the processes of sweetening sour gas and recovery of sulfur and hydrogen are integrated into a single compact process, as described below. First, the sour natural gas stream is contacted with the adsorbent (such as a molecular sieve 5A) in a fluidized bed adsorber, designated as ADS1 in FIG. 2, to effect the removal of H<sub>2</sub>S, H<sub>2</sub>O, and other sulfur-containing contaminants. The partially sweetened natural gas stream is then passed through a second fluidized bed adsorber, designated as ADS2, where CO<sub>2</sub> is stripped, also, using the molecular sieve 5A as an adsorbent. Though, in principle, H<sub>2</sub>S, CO<sub>2</sub>, H<sub>2</sub>O, and other sulfur-containing contaminants can all be removed from the natural gas stream by the molecular sieve 5A in a single adsorber unit, two separate units become necessary for maximizing the process efficiency for sulfur recovery.

The sequential stripping of H<sub>2</sub>S and H<sub>2</sub>O in ADS1 followed by removal of CO<sub>2</sub> in ADS2 is made possible by the well-defined sequence in which these species are adsorbed on the molecular sieve. The residence time and the circulation rates of solids, then will be controlled so that the species adsorbed in ADS1 are primarily H<sub>2</sub>S and H<sub>2</sub>O.

At a high operating pressure (e.g., 1000 psig), the fluidized bed adsorber units can be operated in a bubbling bed mode. Calculations show that these adsorber units can be very compact units, approximately thirty (30") inches in diameter for an eleven (11) MMScfd plant. Existing molecular sieve-based processes employ fixed beds in view of

the possibility of sorbent attrition. The bubbling bed mode of operation (at about three (3) times the minimum fluidization velocity, with a minimum fluidization velocity of approximately thirty-three (33 fps) feet per second at one thousand (1000) psig and three hundred (300°) degrees K for molecular sieves with an average particle diameter of approximately 0.06 inch) reduces the risk of attrition. In addition, a material, such as molybdenum sulfide, PTFE, graphite, among others, with a low coefficient of friction will be added to the bed in very small quantities to further reduce the potential for attrition.

The spent sorbent from the adsorber units is then pneumatically transported to the regeneration units. Regenerators are also operated in the bubbling fluidized bed mode; the temperature of operation is about four hundred and forty (440°) degrees F. The molecular sieve adsorbent from ADS1 is regenerated, with release of  $H_2S$  and  $H_2O$ , in RGN1. This unit is maintained in the bubbling fluidized bed mode using a slip stream from the partially-sweetened natural gas. Calculations show that about 0.5 (%) percent of the natural gas stream will suffice to maintain the operation of RGN1. The mixture of  $H_2S$ ,  $H_2O$ , and natural gas recovered from RGN1 is used for the downstream recovery of elemental sulfur and hydrogen. Spent sorbent from ADS2 is regenerated, with release of  $CO_2$ , in RGN2. The regenerated solids are recirculated into the adsorber units. The ease of sorbent transportation between adsorber and regeneration units is a key advantage of the process of the present invention (in comparison with other fixed dry bed processes) made possible by the use of the fluidized bed mode of operation.

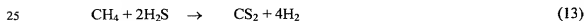
The sorbent recirculation rates are determined by the amount of contaminants in the natural gas. Conventionally, gas-conditioning processes employing molecular sieves are based on fixed bed technology. Cooling and heating of beds to serve as adsorbers or regenerators requires time. The temperature swing adsorption then limits the region of operability to low  $H_2S$  concentrations in medium scale operation. The ability to alter, with ease, the flow rate of solids within the adsorber and regenerator units through operation in the fluidized bed mode provides the process flexibility of operation in the handling of different compositions and greatly enhances the possible regime of operation in terms of  $H_2S$  concentrations as well as processing scale. Since molecular sieves have a high surface area and, therefore, large adsorption capacities, the recirculation rate of solids is kept at a minimum, providing a compact design.

Energy is required to maintain the adsorber/regenerator loops operated on the principle of temperature swing adsorption. The energy to maintain the beds at four hundred and forty (440°) degrees F is supplied by combustion of gases in a pulse

combustor, designated as PC2 and PC3 in FIG. 2, immersed within the gently bubbling fluidized beds. The submerged pulse combustors behave as submerged tubes and therefore deliver the well-known advantage of high heat transfer coefficients (thirty-five (35) to seventy (70)  $\text{BTU hr}^{-1} \text{ft}^{-2} \text{ }^{\circ}\text{F}^{-1}$ ) between the bed and the tubes. These heat transfer coefficients are higher by, at least one order of magnitude in comparison with those obtained from a tube immersed in convective flow of a gas. The higher heat transfer coefficients make possible use of a lower surface area for heat exchange for the same temperature differences and heat duty resulting in a compact design from the regenerator units. The mixing of solids within the bubbling bed ensures that the bed temperature is uniform. The fuel gas for the pulse combustors PC2 and PC3 submerged, respectively, in RGN1 and RGN2, is derived from the synthesis gas ( $\text{CO}$  and  $\text{H}_2$ ) generated in the corona reactor.

In a corona reactor, extremely reactive species, such as radicals and excited molecules are generated at ambient temperature without the presence of catalysts. Also, little energy is lost due to heating of the gas as compared with thermal processes.

The gas mixture, consisting of  $\text{H}_2\text{S}$  and  $\text{H}_2\text{O}$  released from the molecular sieves and natural gas used as the fluidization medium, from RGN1 is used for recovery of elemental sulfur and hydrogen. This recovery is effected in a pulsed corona reactor designated as PCR in FIG. 2. The gas mixture consisting of  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ , and  $\text{CO}_2$ , following expansion, is introduced into the pulsed corona reactor where the following reactions take place:



The efficiency of sulfur recovery according to the present invention depends primarily on minimizing formation of  $\text{CS}_2$  and  $\text{COS}$  in the corona reactor. By adjusting the amount of excess  $\text{CO}_2$ , i.e., the  $\text{H}_2\text{S}/\text{CO}_2$  and  $\text{CH}_4/\text{CO}_2$  ratios, complete conversion of  $\text{H}_2\text{S}$  and  $\text{CH}_4$  is possible. Thus, in a nonthermal plasma reactor,  $\text{H}_2\text{S}$  conversion exceeding ninety-nine (99%) percent is possible.

The gases exiting from the corona reactor consist, mainly, of unconverted  $H_2S$ ,  $CH_4$ , and  $CO_2$ ,  $H_2O$ , elemental sulfur species  $S_I$  with  $I = 1$  to  $8$ ,  $CO$ ,  $H_2$ ,  $CS_2$  and  $COS$ . These gases are quenched, in a condenser designated as COND in FIG. 2, to remove elemental sulfur and water. The remaining gases --  $H_2S$ ,  $CH_4$ ,  $CO_2$ ,  $CO$ ,  $H_2$ ,  $CS_2$ , and  $COS$  -- are compressed back to system pressure (1000 psig for the example considered) before flowing through an adsorption unit, designated as ADS3 in FIG. 2, where the gases also serve as the fluidizing medium for the bubbling bed. The adsorption unit removes  $H_2S$  and  $CO_2$  from the gas stream using the molecular sieve 5A. The spent sorbent from the adsorber unit is regenerated in RGN1 so that the unconverted  $H_2S$  is recycled to the sulfur and hydrogen recovery pulsed corona reactor. The gases from ADS3, consisting of  $CH_4$ ,  $CO$ ,  $H_2$ , and  $COS$ , are passed through a hydrogen separation unit. The rest of the gas mixture is fired in pulse combustors PC2 and PC3, which provide the energy required to maintain the regenerators RGN1 and RGN2 at the temperature of four hundred and forty ( $440^\circ$ ) degrees F. It should be noted that a fraction of the gas stream exiting the hydrogen separator is used for fluidization of RGN2 after which the gases are fired in PC3. The off-gases from PC2 and PC3, following heat recovery, are vented.

In comparison with some of the existing processes, there are several advantages offered by the process configuration of the present invention including, but not limited to, recovery of elemental sulfur and hydrogen, smaller size and lower costs, energy efficiency, flexibility of operation for treatment of sour gas and Claus reactor effluent streams with varying  $H_2S$  levels, etc.

First, concerning the recovery of elemental sulfur and hydrogen, the off-gas from the regenerator is sent to the flare in conventional fixed bed processes. In the system and process according to the present application, both elemental sulfur and hydrogen are recovered from  $H_2S$  in the sour gas.

Second, the system and process according to the present invention provides smaller size and lower costs. Conventional technology employs fixed bed adsorption/regeneration columns such that when the adsorber column gets exhausted, flow of "sour" gas is diverted to another adsorber column. The exhausted adsorber column is then regenerated by passage of hot gas. After regeneration, this column has to be cooled to the temperatures at which the molecular sieves will adsorb the contaminants again. Since the cooling of the bed takes time, conventional processes often require three (3) or four (4) columns. In the system and process of the present application, regenerated sorbent is recycled continuously. In addition, the thermal inertia and the excellent mixing

characteristics in the two legs of the recirculating bed ensure that the temperatures are maintained at the levels required. Consequently, only two columns will be necessary.

Third, the system and process according to the present invention provides energy efficiency. In conventional processes, the energy required to raise the temperature of the molecular sieves to strip the contaminants is provided by combustion of a natural gas stream in a separate burner. The off-gases from the regenerator are sent to the flare. In this process, the synthesis gas generated from  $H_2S$  in the corona reactor is burnt in pulse combustors and the regenerator is heated through the pulse combustors acting as immersed heat transfer tubes. Thus, the process makes use of the high heat transfer coefficients provided by submerged tubes in a fluidized bed. Also, the energy required to raise the bed temperature is obtained, indirectly, from  $H_2S$ .

Finally, the system and process of the present application provides flexibility of operation. The sorbent recirculation rate can be adjusted to meet different levels of contamination in the natural gas. Calculations show that the process can sweeten sour gas of the composition (one (1%) percent  $H_2S$ ) with sulfur recovery of ninety-nine (99%) percent. The operating conditions identified by the thermodynamic calculations -- in terms of higher  $H_2S/CO_2$  ratios aiding higher sulfur recovery -- suggest that the proposed process can be used to advantage for conditioning of gas streams with higher  $H_2S$  contents. Conventionally, gas-conditioning processes employing molecular sieves are based on fixed bed technology. Cooling and heating of beds to serve as adsorbers or regenerators requires time. The temperature swing adsorption then limits the region of operability to low  $H_2S$  concentrations in medium scale operations. The ability to alter, with ease, the flow rate of solids within the adsorber and regenerator units through handling of different compositions and greatly enhances the possible regime of operation in terms of  $H_2S$  concentrations as well as processing scale.

The foregoing exemplary descriptions and the illustrative preferred embodiments of the present invention have been explained in the drawings and described in detail, with varying modifications and alternative embodiments being taught. While the invention has been so shown, described and illustrated, it should be understood by those skilled in the art that equivalent changes in form and detail may be made therein without departing from the true spirit and scope of the invention, and that the scope of the present invention is to be limited only to the claims except as precluded by the prior art. Moreover, the invention as disclosed herein, may be suitably practiced in the absence of the specific elements which are disclosed herein.



# CLAIMS

We claim:

1. A device for removing contaminants from a natural gas stream, the device comprising:

first adsorbent means positioned within a first fluidized bed operating at a first predetermined temperature for removing at least a portion of the contaminants from the natural gas stream and creating a sweetened natural gas stream and a spent sorbent; and

second adsorbent means positioned within a second fluidized bed operating at a second predetermined temperature for receiving the spent sorbent from the first adsorbent means, the second adsorbent means removing the contaminants from the spent sorbent and circulating regenerated sorbent to the first adsorbent means.

2. The device of claim 1 wherein the contaminants are selected from the group consisting of  $H_2S$ ,  $CO_2$ , and  $H_2O$ .
3. The device of claim 1 wherein the first adsorbent means is a fluidized bed absorber having a molecular sieve.
4. The device of claim 1 wherein the second adsorbent means is a fluidized bed regenerator having a molecular sieve.
5. The device of claim 1 wherein the second predetermined temperature is greater than the first predetermined temperature.
6. The device of claim 1 wherein the first predetermined temperature is between approximately twenty ( $20^\circ$ ) degrees C and approximately sixty ( $60^\circ$ ) degrees C.
7. The device of claim 6 wherein the first predetermined temperature is approximately twenty-five ( $25^\circ$ ) degrees C.

8. The device of claim 1 wherein the second predetermined temperature is between approximately one hundred (100°) degrees C and approximately three hundred (300°) degrees C.
9. The device of claim 1 wherein the second predetermined temperature is approximately two hundred (200°) degrees C.
10. The device of claim 1 and further comprising:  
conversion means for converting H<sub>2</sub>S within the removed contaminants to elemental sulfur and hydrogen at a predetermined temperature less than approximately four hundred (400°) degrees C.
11. The device of claim 10 wherein the conversion means is a nonthermal plasma corona reactor.
12. An apparatus for converting H<sub>2</sub>S to elemental sulfur and hydrogen, the apparatus comprising:  
conversion means for receiving H<sub>2</sub>S and for converting H<sub>2</sub>S to elemental sulfur and hydrogen at a predetermined temperature less than approximately four hundred (400°) degrees C.
13. The apparatus of claim 12 wherein the conversion means is a nonthermal plasma corona reactor.
14. The apparatus of claim 12 and further comprising:  
adsorbent means positioned within a fluidized bed for removing at least a portion of H<sub>2</sub>S from a natural gas stream; and  
means for providing the removed H<sub>2</sub>S to the conversion means.
15. The apparatus of claim 14 wherein the adsorbent means includes a first adsorbent having a first predetermined temperature and second adsorbent having a second predetermined temperature.

16. The apparatus of claim 15 wherein the first adsorbent and the second adsorbent are a molecular sieves.
17. The apparatus of claim 15 wherein the second predetermined temperature is greater than the first predetermined temperature.
18. A method for removing  $H_2S$  and other contaminants from a natural gas stream and converting  $H_2S$  to elemental sulfur and hydrogen, the method comprising:
- providing first adsorbent means;
  - positioning the first adsorbent means within a fluidized bed at a first predetermined temperature;
  - introducing the natural gas stream to the first adsorbent means thereby removing at least a portion of the  $H_2S$  and other contaminants from the natural gas stream and creating a sweetened natural gas stream and a spent sorbent;
  - providing second adsorbent means;
  - positioning the second adsorbent means within a fluidized bed at a second predetermined temperature;
  - introducing the spent sorbent from the first adsorbent means to the second adsorbent means thereby removing the contaminants from the spent sorbents and creating a regenerated sorbent;
  - recirculating the regenerated sorbent from the second adsorbent means to the first adsorbent means;
  - providing a nonthermal plasma reactor;
  - introducing the removed contaminants from the second adsorbent means to the nonthermal plasma reactor; and
  - converting the  $H_2S$  to elemental sulfur and hydrogen at a third predetermined temperature.
19. The method of claim 18 wherein the first adsorbent means is a fluidized bed adsorber having a molecular sieve and the second adsorbent means is a fluidized bed regenerator having a molecular sieves.

20. The method of claim 18 wherein the second predetermined temperature being greater than the first predetermined temperature.

21. The method of claim 18 wherein the first predetermined temperature being between approximately twenty (20°) degrees C and approximately sixty (60°) degrees C.

22. The method of claim 18 wherein the second predetermined temperature being between approximately one hundred (100°) degrees C and approximately three hundred (300°) degrees C.

23. The method of claim 18 wherein the third predetermined temperature being less than approximately four hundred (400°) degrees C.